

**STUDIES ON THE PERSISTENCE AND LEACHING IN SOIL
OF NEMATICIDES HAVING USE IN FLOWER BULB PRODUCTION IN
HUMBOLDT AND DEL NORTE COUNTIES, CALIFORNIA
I. PHORATE AND ETHOPROP**

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I. PHORATE AND ETHOPROP.

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DECEMBER, 1988

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ABSTRACT

Small plots were established in commercial daffodil flower production fields in Del Norte and Humboldt Counties to study the persistence and leaching of phorate, an insecticide-nematicide currently used in flower bulb production, and ethoprop, a nematicide that has potential for future use. Phorate was applied as a granular formulation 4 to 6 inches deep in soil of each plot in September, 1987. Ethoprop was similarly applied as a granular material in the Del Norte County plot and as a liquid in the Humboldt County plot. Two replicate soil cores were collected from each plot at 1 day, 57 days, 181 days and 237 days after application using a bucket auger. The depth sampled began at 1 foot on day 1 and increased to 5 feet at 6 inch intervals on day 237 after application. Phorate residues in the zone of application decreased dramatically during the 8 month study period. Oxidation of phorate to the sulfoxide and sulfone breakdown products increased over time and concentrations of the two oxidation products accounted for 84 to 96 % of the total pesticide residue found in the last samples. The two compounds were much more mobile than the parent phorate in both plots, especially in Humboldt County where the soil was much sandier and porous than in Del Norte County. Residues of phorate were found at a maximum depth of 45 inches in Del Norte County and 60 inches in Humboldt County. Ethoprop degraded to low levels in both plots during the 8 month study period; the type of formulation used on the plots did not appear to cause great differences in persistence or leaching. Ethoprop residues were found at maximum sampling depths of 48 inches (Del Norte County) and 54 inches (Humboldt County) in the plots. Heavy rainfall, 37 inches at the Humboldt County plot and 50 inches at the Del Norte

County plot, that fell during the study period was probably responsible for leaching of the two nematicides.

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DISCLAIMER

The mention of commercial products, their source or use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

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INTRODUCTION

The production of high quality flower bulbs in areas of Del Norte and Humboldt Counties is dependent upon the availability of pesticides that can protect the bulbs from nematode damage. However, the number of effective nematicides available to growers is dwindling rapidly. During the past few years, uses of two effective nematicides, aldicarb and 1,2-dichloropropane, were cancelled or restricted because residues were found in groundwater. They were replaced by 1,3-dichloropropene (Telone II) used as a preplant fumigation and by fenamiphos (Nemacur) applied at planting. However, the manufacturer recently cancelled label uses of fenamiphos on bulb crops in the two counties because it was found to be leaching in soils of lily bulb fields (8).

Contamination of groundwater by soil applied pesticides in the two counties can be attributed to the combination of porous soils, high rainfall and occasional high water tables that exist there. Despite these conditions, the need for effective nematicides will probably continue. Phorate (Thimet), a nematicide-insecticide that was used for several years prior to aldicarb, has again become a choice for nematode control on bulb crops. Another nematicide-insecticide, ethoprop (Mocap) also has potential for use. It is important to determine the persistence and leaching potential of nematicides to be used in these bulb production areas.

This study was conducted to measure the persistence and movement of these two chemicals in anticipation of heavy use of phorate during the next several years and potential use of ethoprop on bulb crops. Information gathered

from this study may be useful in determining the suitability of these chemicals in soils of bulb production areas of Del Norte and Humboldt counties.

MATERIALS AND METHODS

Humboldt County Plot

The plot, located near McKinleyville, was in a field used for commercial daffodil flower production. Bulbs had been planted in raised beds spaced 42 inches apart late in the summer of 1987 and no nematicides were applied to the field. The soil was an Arcata loam, 0-3 % slope (4). A 22-foot-long portion of one row located in the northwest quadrant of the field was staked off into two 10-foot-long sections separated by a 2-foot-long space; one section of the plot would later be treated with phorate and the other with ethoprop.

Before the pesticides were applied, a background core was taken from the space between the two sections. A 3 1/2-inch diameter bucket auger was used to collect soil at 6-inch intervals from the surface down to a depth of 9 feet. Soil from each interval was mixed in a polyethylene bag and approximately 1 pint was saved in a separate bag for measurements of pH, organic carbon content and particle size analysis. Methods used for measurements of soil properties have been described (8).

In preparation for the application of the nematicides to the plots, a spade was used to scrape off the top 4 to 6 inches of soil from the planting bed in each plot. This left an exposed area of soil approximately 12 inches wide by 10 feet long. The ethoprop formulation used was Mocap 70% liquid, with a recommended label rate of 2 quarts per acre (1.44 ml per 10 feet of row). In order to insure the presence of sufficient levels to study potential leaching, we applied 3.0 ml of the Mocap mixed in 750 ml of tap water. The mixture was sprayed onto the soil using a Hudson sprayer with the spray nozzle held

approximately 6 inches above the soil. During the application, the nozzle was repeatedly moved over the exposed soil surface until all liquid had been used. Finally, soil that had been removed was spread over the treated area to a depth of 4 to 6 inches, levelled and packed down with the shovel blade.

The phorate plot was prepared in the same manner described above. A granular formulation (Thimet 15 G) was used at the label rate of 45 lbs/acre (15.5 gm per 10 feet of treated row). The granules were sprinkled over the exposed soil surface using a large metal salt shaker with holes large enough to allow the granules to pass through. After application, the treated area was covered with soil and packed down as before.

The soil had a 9-11.7 % moisture content in the top 12 inches and no water was applied before the first soil cores were collected approximately 18 hours after treatment.

Records of local rainfall that occurred during the study period were obtained from the U. S. Forest Service nursery located approximately 2.5 miles northeast of the study plot.

Del Norte County Plot

The plot was established in a commercial daffodil field located near Fort Dick, CA. Bulbs had been planted in raised beds spaced 42 inches apart in the summer of 1987; no nematicides had been applied. The soil was a shallow Carlotta loam, 0-3 % slope (4). A plot 22 feet long was marked off, but in this case it was located in the space between two rows near the northwest corner of the field. A background core was collected at 6-inch intervals from

the surface down to 4 feet from the 2-foot-long area located between the two plots. Attempts to collect deeper samples were prevented by the presence of cobbles. The samples were saved for measurements of pH, organic carbon content and particle size analysis. A shovel was used to loosen the soil to an 8-inch depth in an area 12-14 inches wide in the two plots. Then the top 4 to 6 inches of soil was scraped off to one side.

A granular formulation of ethoprop (Mocap 10 G) was used instead of the liquid formulation that was applied in the Humboldt County plot. We had intended to also use the granular formulation in the Humboldt County plot but it was not available in time. Thirty grams of Mocap 10 G was sprinkled over a 10-inch wide band of soil in the plot. The phorate plot was treated with 15.5 gm of Thimet 15 G as was done in the Humboldt County plot. The treated areas were covered with 4 to 6 inches of soil and packed down with a shovel blade.

The moisture content in the top 12 inches of soil in the plots ranged from 10 to 15 % at the time they were treated. No water was applied before the first soil cores were collected approximately 18 hours after treatment. Records of local rainfall that occurred during the study period were obtained from the Pacific Power Co. located approximately 10 miles south of the test plot.

Soil Sample Collection

Soil coring was accomplished with a 3 1/2-inch diameter bucket auger. Before each sample was collected, the bucket auger was washed in laboratory detergent mixed with water, rinsed with tap water, rinsed with laboratory grade propanol and finally rinsed with distilled water. After the auger had gone 6 inches into the ground, it was withdrawn and loose soil was knocked from each end and

discarded. The remaining soil was knocked into a clean polyethylene bag, thoroughly mixed, and enough poured into a 1 pint screw cap jar to fill it. The jar was sealed with a foil-lined lid and placed on dry ice. Samples were kept frozen until ready for extraction.

After the first 12 inches of soil were removed, a 16-inch-long stainless steel sleeve with an inside diameter slightly larger than 3 1/2 inches was inserted into the hole to a depth of 12 inches. The sleeve served to prevent soil from falling into the hole while deeper sampling was conducted. Coring was then resumed by sampling down through the sleeve. Each hole was refilled with the excess soil after coring was completed; additional soil was taken from a nearby bed when necessary. A small flag was used to mark the location of each site where a core had been sampled in the treatment area.

Two replicate soil cores were to be collected at 1 day, and then approximately 2 months, 6 months and 8 months post application from each plot. Soil cores were taken to depths of 12 inches and 36 inches at the 1 day post and 2 month post application samplings, respectively. It was planned to collect deeper samples at each successive sampling but the presence of rocks in the soil of both plots sometimes made that impossible.

Chemical Analysis

The primary laboratory that conducted the pesticide analyses was the California Department of Food and Agriculture's (CDFA) Chemistry Laboratory Services Branch located in Sacramento, California. Quality control analysis of split samples was conducted by Enseco-California Analytical Laboratory (CAL) located in West Sacramento, California. Soil samples were analyzed

for residues of ethoprop, phorate, phorate sulfoxide and phorate sulfone. Samples were extracted with acetone and quantified by gas chromatography (GC) with a nitrogen phosphorous (NP) detector (Appendix A.).

For methods development, replicates of blank soil samples were spiked (blank matrix spikes) with ethoprop and phorate at 40, 600 and 6000 ppb, and with phorate sulfoxide and phorate sulfone at 40 and 600 ppb. The detection limits, mean percent recoveries, and standard deviations (SD) for ethoprop, phorate, phorate sulfoxide and phorate sulfone were 0.006 ppm, 103 percent ± 10.5 , 0.012 ppm, 102 percent ± 6.2 , 0.012 ppm, 82 percent ± 11 , and 0.012 ppm, 60 percent ± 9.7 , respectively (Appendix B, Tables 1, 2, 3). The mean percent recovery and SD were used to calculate the warning limits (± 2 SD from mean) and control limits (± 3 SD from mean) for accuracy.

For continuous quality control during analysis a blank matrix and blank matrix spike for each chemical were analyzed with each extraction set (Appendix B, Tables 4,5). One out of seven matrix spike recoveries fell outside the lower control limit set for phorate at 83% and one fell outside the upper control limit set for phorate sulfone at 98% (Appendix B, Table 5). No corrective action was taken.

Split sample interlaboratory analyses were conducted twice during the study, once in the winter of 1987 and again in Spring 1988. The Winter 1987 split data showed positive levels for ethoprop, phorate, phorate sulfoxide and phorate sulfone. Ethoprop was found in five out of the six samples analyzed by CDFA laboratory, while CAL showed positive ethoprop levels for only four out of the six samples (Appendix B, Table 6). The detection limits set by

CDFA and CAL laboratories at 0.006 ppm and 0.04 ppm, respectively, might have accounted for the positive ethoprop level found by CDFA and not by CAL laboratory. Only one soil split sample showed non-detected levels by both laboratories for residues of phorate, phorate sulfoxide and phorate sulfone (Appendix B, Tables 7,8).

The Spring 1988 data for quality control samples split between laboratories also showed positive levels for ethoprop, phorate, phorate sulfoxide and phorate sulfone. The mean ethoprop level, SD and coefficient of variation (CV) between the two laboratories ranged from 0.09 ppm to 2.6 ppm, 0.01 to 0.59, and 3.6% to 34% (Appendix B, Table 9). Phorate was found in all six samples analyzed by CDFA laboratory, while CAL showed positive phorate levels for only five out of the six samples (Appendix B, Table 10). The positive phorate level found by CDFA laboratory was well above both detection limits. The mean phorate sulfoxide and phorate sulfone levels, SD and CV between the two laboratories ranged from 0.86 ppm to 5.6 ppm, 0.03 to 3.0, and 3.3% to 105 %, and 0.93 ppm to 6.4 ppm, 0.11 to 2.0 and 12% to 54%, respectively (Appendix B, Table 11).

A storage dissipation study was conducted to measure anticipated breakdown of ethoprop and phorate to its metabolites over the duration of chemical analyses. Twelve replicate blank matrix spike samples were prepared on October 16, 1987, each containing 1 ppm of ethoprop and phorate in 1 liter of distilled water. Three spikes were analyzed on day 0, 47, 160, and 220 for each chemical. There was no significant breakdown of ethoprop over the 220 days; however, phorate began to break down to sulfoxide around day 47 and

continued dissipating over the storage period of 220 days (Appendix B, Tables 12, 13, 14).

RESULTS AND DISCUSSION

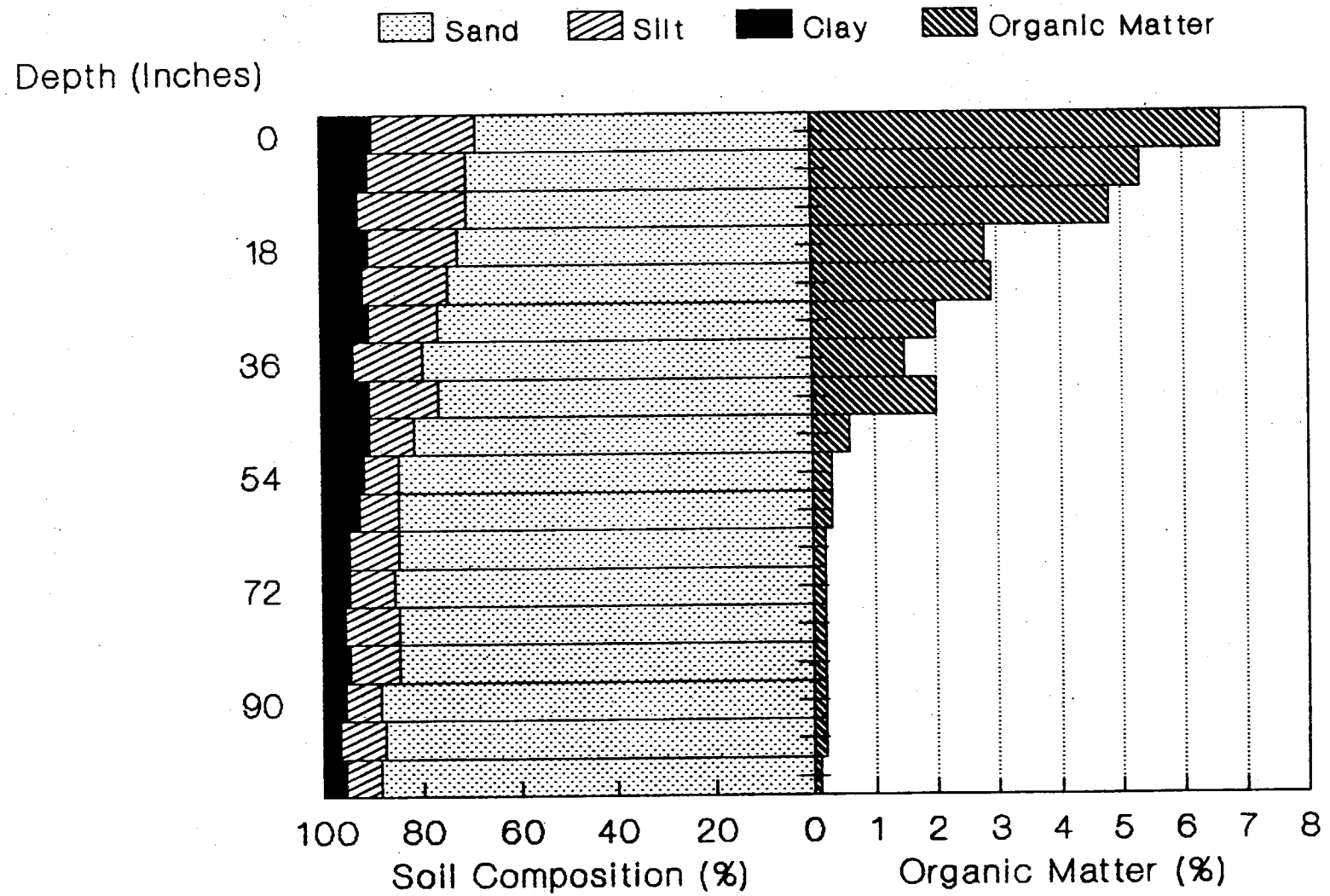
Phorate

The results obtained from our study plots located in two northwestern California counties showed that phorate (Thimet) was largely converted to the sulfoxide and sulfone compounds during the 8 month study period. Moreover, the sulfoxide and sulfone compounds leached through soil much more readily than the parent phorate compound.

The Humboldt County plot consisted of Arcata loam soil that had a pH range of 4.7 to 5.9 and contained more than 68 % sand throughout the 9 -foot-deep background core with lesser amounts of silt (7 to 22 %) and clay (3.4 to 10.4 %; Figure 1). Organic carbon content ranged from 4.8 to 6.6 % in the upper 18 inches of soil, dropped off to 1.5 to 2.9 % in the next 30 inches and then tapered off to 0.1 to 0.6 %.

Total phorate residues (combined total of phorate, sulfoxide and sulfone) in the top 6 inches of soil (treated area) decreased during the study period from an average of 50 ppm on the day after application to 12.3 ppm almost 8 months later (Figure 2). As expected, high (28.1 to 68.0 ppm) concentrations of phorate parent compound were found in the top 6 inches of soil 1 day after application (Table 1). Phorate residues were later found at a maximum depth range of 18-24 inches, 57 days and 181 days post application (Tables 2, 3). At the next sampling, 237 days post application, phorate was found at a maximum depth of 12 inches except for one deeper positive sample in each core (Table 4). Due to an error, the steel sleeve was not used to collect cores on

Figure 1. Measurement of particle size characteristics (composition) and organic matter content of background soil samples collected from the test plot in Humboldt County.



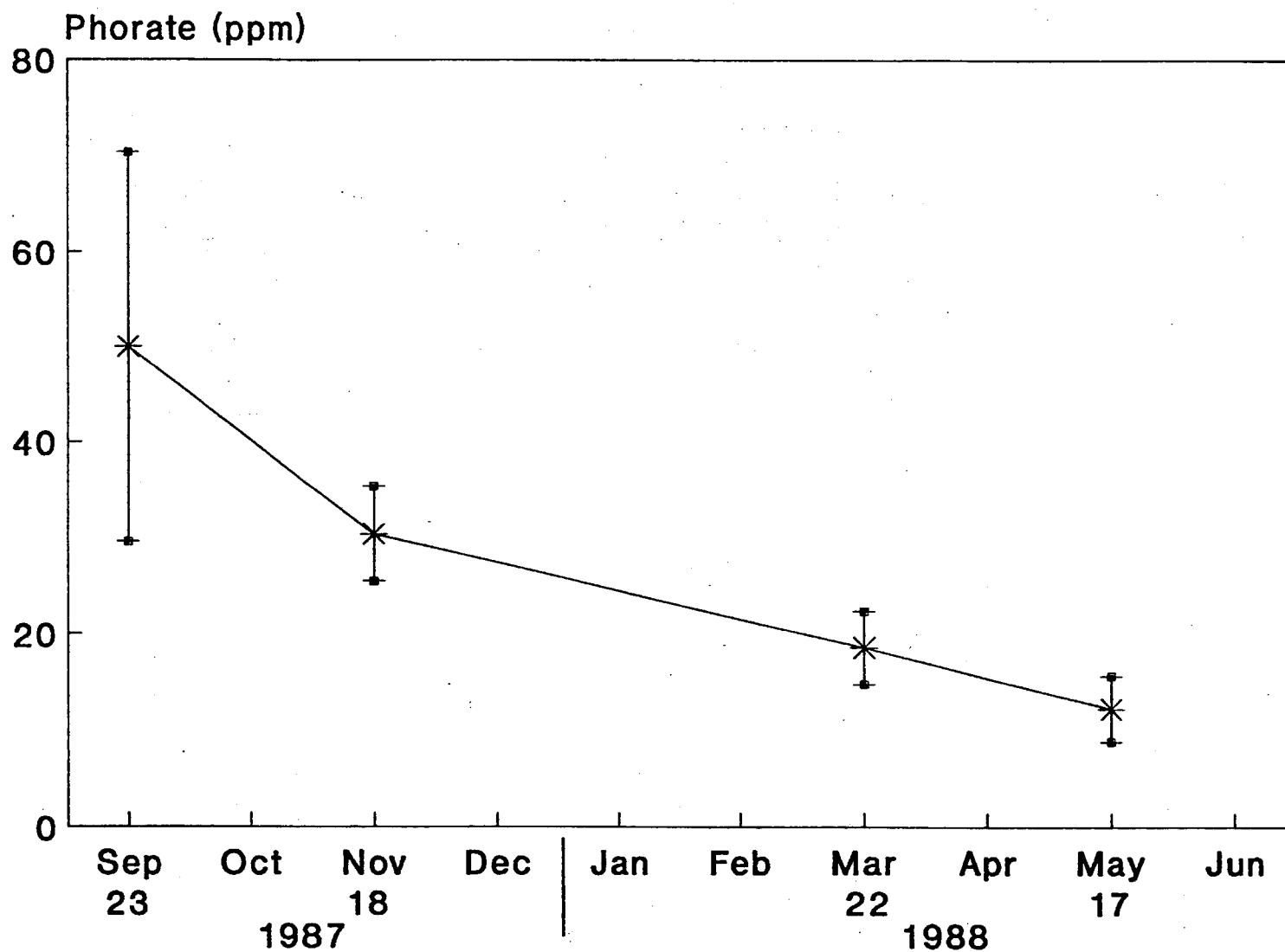


Figure 2. Mean and range of total phorate residues present in the top 6 inches of soil in two cores collected on four sampling dates from the test plot in Humboldt County.

Table 1. Concentrations of phorate residues in soil core samples collected on September 23, 1987, 1 day post application from a plot located in Humboldt County.

Depth (inches)	<u>Phorate (ppm) expressed as total residue and phorate (P), sulfoxide (SO), and sulfone (SO2)</u>							
	Core 1				Core 2			
	Total	P	SO	SO2	Total	P	SO	SO2
0 - 6	29.54	28.10	1.32	0.12	70.30	68.00	2.22	0.08
6 - 12	0.52	0.41	0.10	0.01	3.01	2.44	0.23	0.34
Cumulative total	30.06	28.51	1.42	0.13	73.31	70.44	2.45	0.42

Table 2. Concentrations of phorate residues in soil core samples collected on November 18, 1987, 57 days post application from a plot located in Humboldt County.

Depth (inches)	Phorate (ppm) expressed as total residue and phorate (P), sulfoxide (SO), and sulfone (SO2)							
	Core 1				Core 2			
	Total	P	SO	SO2	Total	P	SO	SO2
0 - 6	35.40	29.10	4.14	2.16	25.42	20.20	3.20	2.02
6 - 12	0.59	0.36	0.15	0.08	0.34	0.19	0.09	0.06
12 - 18	3.83	3.10	0.56	0.17	3.34	2.06	0.94	0.34
18 - 24	1.44	1.26	0.14	0.04	a			
					ND	ND	ND	ND
24 - 30	ND	ND	ND	ND	ND	ND	ND	ND
30 - 36	ND	ND	ND	ND	ND	ND	ND	ND
Cumulative total	41.26	33.82	4.99	2.45	29.10	22.45	4.23	2.42

a. None detected; minimum detectable level was 0.02 ppm for phorate, 0.009 ppm for phorate sulfoxide and 0.003 ppm for phorate sulfone.

Table 3. Concentrations of phorate residues in soil core samples collected on March 22, 1988, 181 days post application from a plot located in Humboldt County.

Depth (inches)	Phorate (ppm) expressed as total residue and phorate (P), sulfoxide (SO), and sulfone (SO ₂)							
	Core 1				Core 2			
	Total	P	SO	SO ₂	Total	P	SO	SO ₂
0 - 6	14.84	3.81	5.17	5.86	22.37	8.15	7.79	6.43
6 - 12	0.98	0.04	0.22	0.72	6.80	0.24	3.00	3.56
12 - 18	1.98	0.01	0.96	1.01	4.25	0.12	1.92	2.21
18 - 24	0.56	^a ND	0.33	0.23	1.02	0.02	0.52	0.48
24 - 30	0.04	ND	0.02	0.02	0.14	ND	0.09	0.05
30 - 36	ND	ND	ND	ND	0.04	ND	0.02	0.02
36 - 42	0.02	ND	0.01	0.01	0.04	ND	0.02	0.02
42 - 48	ND	ND	ND	ND	0.02	ND	0.01	0.01
48 - 54	0.33	ND	0.03	0.30	ND	ND	ND	ND
Cum. total	18.75	3.86	6.74	8.15	34.68	8.53	13.37	12.78

a. None detected; minimum detectable level was 0.01 ppm for phorate and phorate sulfoxide and 0.005 ppm for phorate sulfone.

Table 4. Concentrations of phorate residues in soil core samples collected on May 17, 1988, 237 days post application from a plot located in Humboldt County. Stainless steel sleeve was not used on this date.

Depth (inches)	Phorate (ppm) expressed as total residue and phorate (P), sulfoxide (SO), and sulfone (SO ₂)							
	Core 1				Core 2			
	Total	P	SO	SO ₂	Total	P	SO	SO ₂
0 - 6	15.64	3.42	5.72	6.50	8.87	0.95	3.09	4.83
6 - 12	3.39	0.06	1.15	2.18	11.39	0.14	5.25	6.00
12 - 18	1.64	ND	0.52	1.12	1.27	ND	0.34	0.93
18 - 24	0.13	ND	0.05	0.08	0.01	ND	ND	0.01
24 - 30	0.13	ND	0.04	0.09	0.12	ND	0.05	0.07
30 - 36	0.50	0.08	0.16	0.26	0.14	ND	0.06	0.08
36 - 42	0.11	ND	0.05	0.06	0.04	ND	0.02	0.02
42 - 48	0.12	ND	0.05	0.07	0.01	ND	ND	0.01
48 - 54	ND	ND	ND	ND	0.15	0.02	0.05	0.08
54 - 60	0.04	ND	0.04	ND	ND	ND	ND	ND
Cumulative total	21.70	3.56	7.78	10.36	22.00	1.11	8.86	12.03

a. None detected; minimum detectable level was 0.01 ppm for phorate, phorate sulfoxide and phorate sulfone.

that date so that the first foot of the core hole was not sealed off as it had been for all previous sampling. It is possible that the two deeper positive samples occurred due to leaching or, they may have resulted from contamination from shallower levels.

There was a rapidly increasing rate of conversion of phorate to the sulfoxide and sulfone oxidation products as time progressed (Figure 3) accompanied by leaching of the two oxidation products into the soil profile (Tables 1-4). The cumulative total concentration of parent compound present in replicate cores decreased from an average value of 49.48 ppm at 1 day post application to only 2.34 ppm at 237 days post application. Conversely, average concentrations of phorate sulfoxide and sulfone increased from 1.94 and 0.28 ppm to 8.32 and 11.20 ppm, respectively, during the same period of time.

Residues of the sulfoxide and sulfone leached to a maximum depth of 24 inches 57 days after application (November 18) and then moved as deep as 54 inches and 60 inches at 181 (March 22) and 237 days (May 17) post application, respectively. The sulfoxide and sulfone were present in most of the core segments collected on the two latter dates. Most of the rainfall occurred in the study area during December and January with lesser amounts in November and February through May (Figure 4). Approximately 3.5 inches fell during the period between phorate application and the sampling in November. More than 28 additional inches of rainfall occurred before the next sampling in March and 5.5 more inches of rain fell before the final sampling in May. Those high amounts of rainfall probably were responsible for the leaching of sulfoxide and sulfone that was evident in cores collected in March and May.

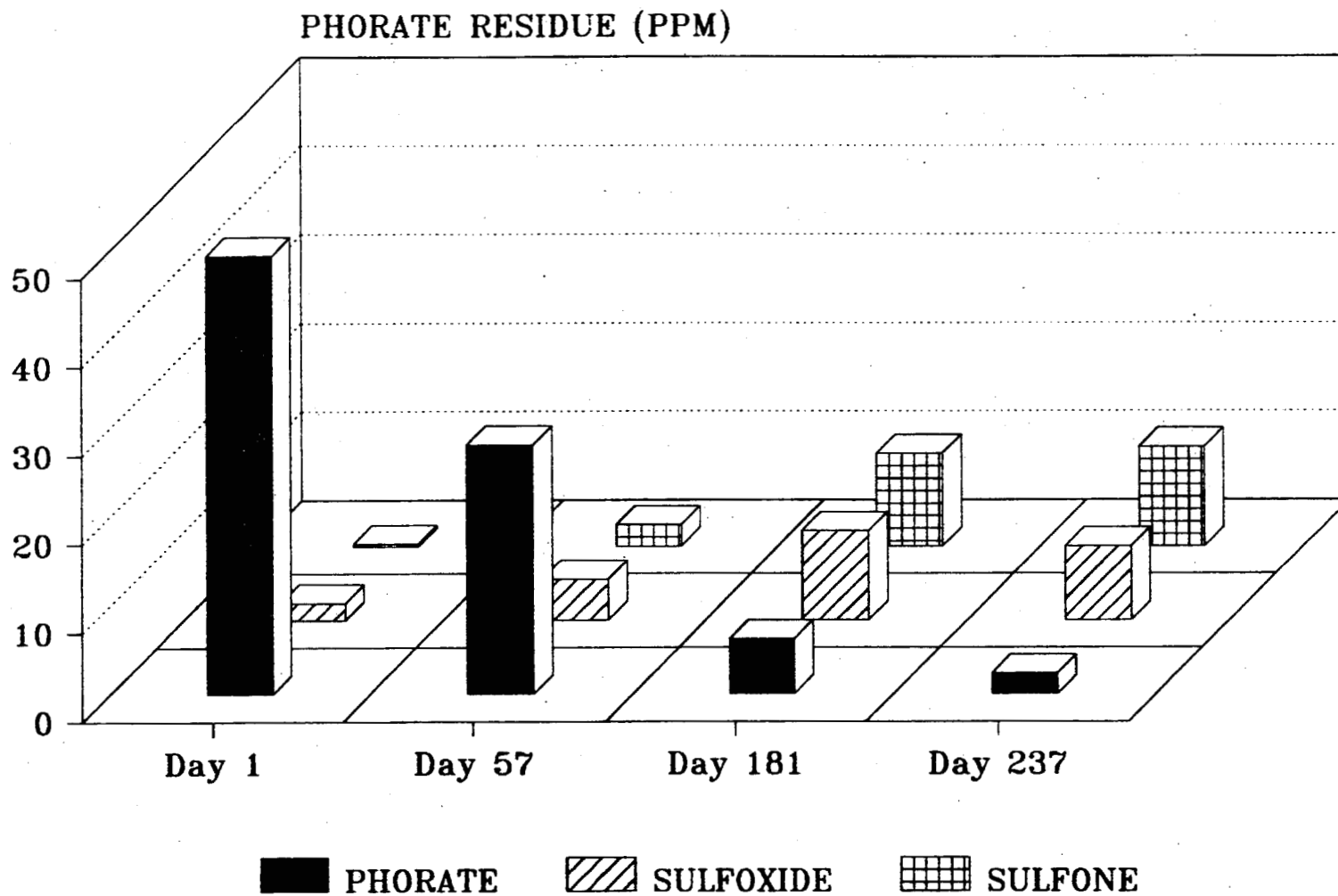


Figure 3. Average cumulative concentrations of phorate, phorate sulfoxide and phorate sulfone present in two soil cores collected on specified numbers of days post application from the test plot in Humboldt County.

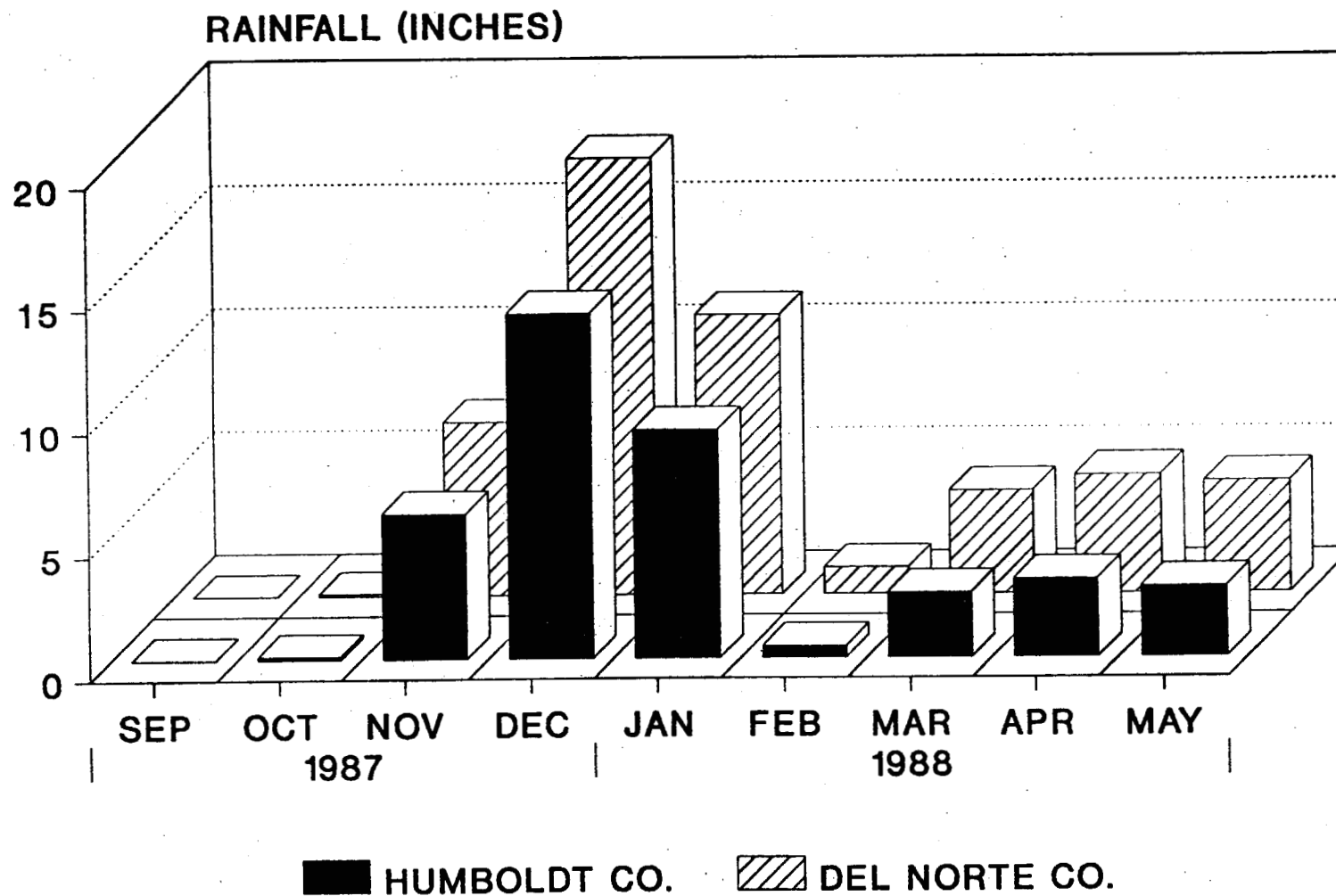


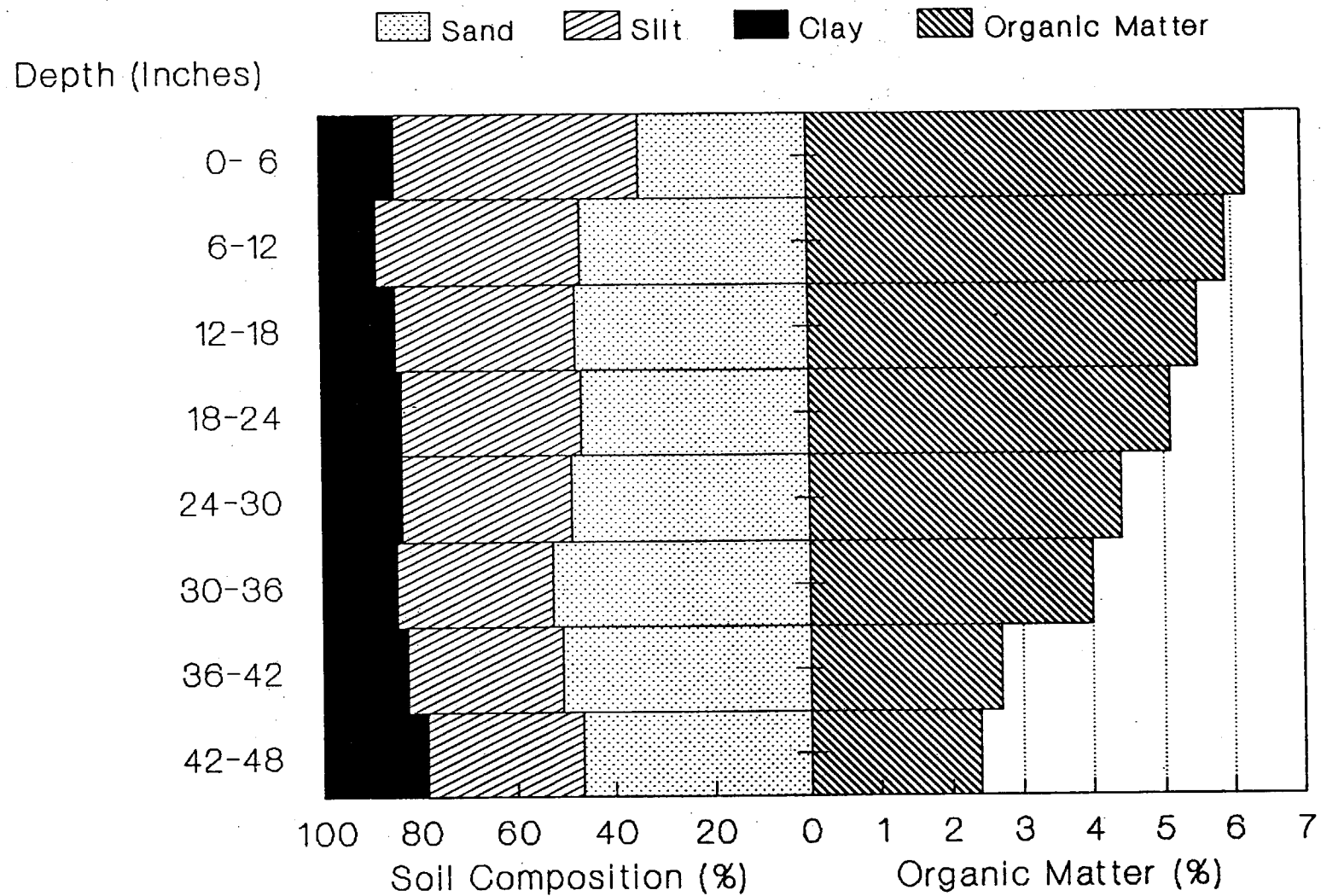
Figure 4. Amounts of monthly rainfall that were recorded from 9/24/87 to 5/18/88 at locations near test plots in Humboldt and Del Norte Counties.

As was mentioned earlier, the stainless steel sleeve used to prevent soil from the upper 12 inches from falling into the hole as coring progressed, was not available for use during sampling in May. Thus, there was a greater possibility of contamination at that time than in previous sampling from the plot. The data from Tables 3 and 4 show that the distribution of soil samples containing phorate residues was very similar for the cores collected in March and May. The absence of the sleeve appeared to have little effect on the results for samples collected in May.

The Carlotta loam soil in the Del Norte County plot contained gravel which made sampling difficult or impossible at certain depths. Thus, cores taken from that plot in March and May were much shallower than those from Humboldt County and deeper samples could not always be taken on successive sampling dates. The soil contained similar proportions of sand (35 to 53 %) and silt (32 to 50 %) with lesser amounts of clay (11 to 21 %) in the profile (Figure 5). Soil pH ranged from 5.4 to 6.0 and the organic carbon content was moderately high ranging from 6.2 % near the surface to 2.4 % in the deepest background core sample at 48 inches.

Total phorate residues in the top 6 inches of soil decreased during the study period from an average of 26 ppm on the day after application to 8.9 ppm at the last sampling made nearly 8 months later (Figure 6). High initial concentrations (7.13 to 22.50 ppm) of phorate parent compound were found in the top 6 inches of soil 1 day after application (Table 5). Residues in two replicate cores were later found at maximum depths of 18 and 36 inches 57 days post application (Table 6), but only 12 inches and 6 inches deep at 182 days and 237 days post application, respectively (Tables 7, 8).

Figure 5. Measurement of particle size characteristics (composition) and organic matter content of background soil samples collected from the test plot in Del Norte County.



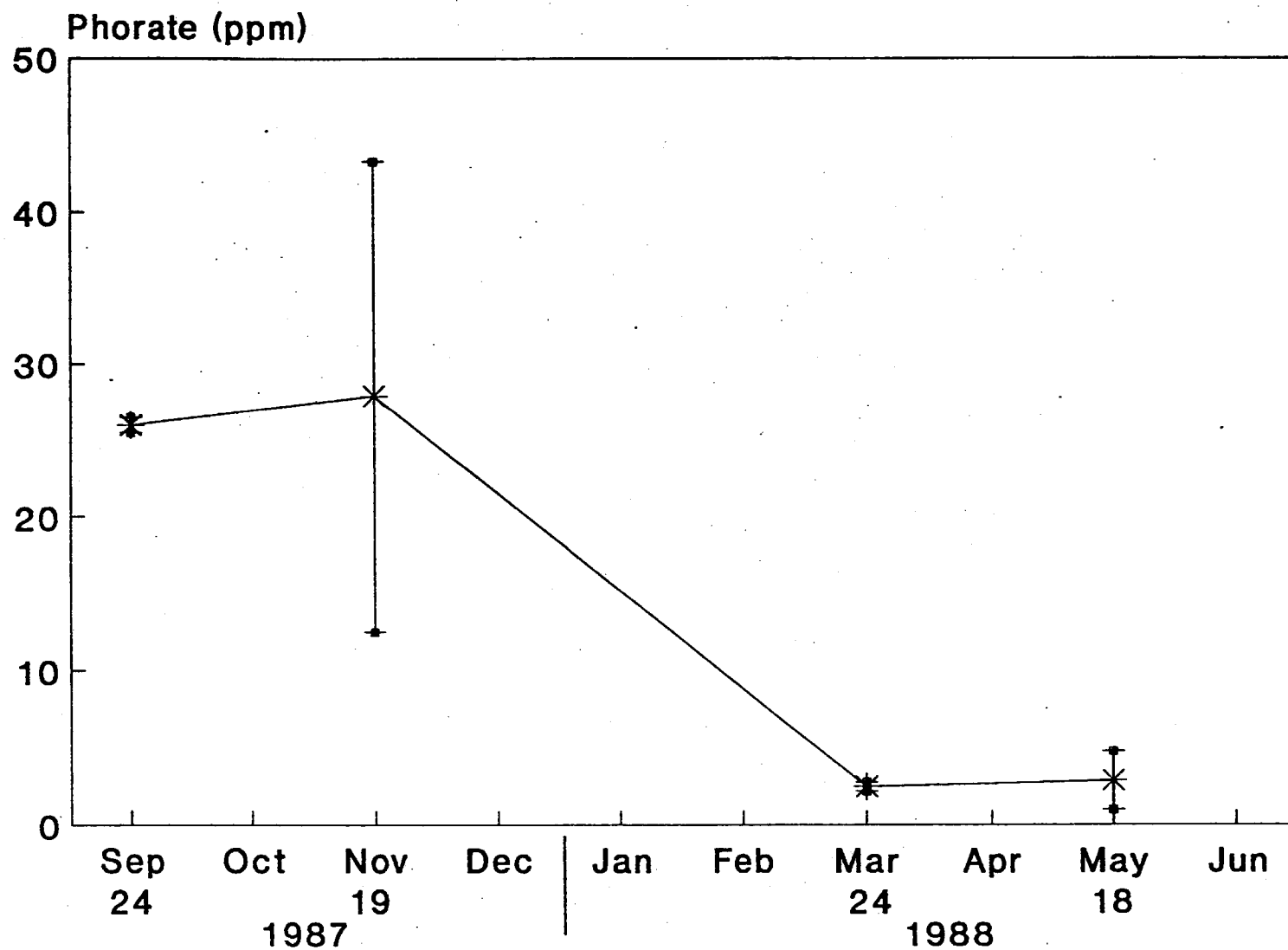


Figure 6. Mean and range of total phorate residues present in the top 6 inches of soil in two cores collected on four sampling dates from the test plot in Del Norte Norte County.

Table 5. Concentrations of phorate residues in soil core samples collected on September 24, 1987, 1 day post application from a plot located in Del Norte County.

Depth (inches)	<u>Phorate (ppm) expressed as total residue and phorate (P), sulfoxide (SO), and sulfone (SO2)</u>							
	Core 1				Core 2			
	Total	P	SO	SO2	Total	P	SO	SO2
0 - 6	25.50	21.50	3.20	0.80	26.49	22.50	3.19	0.80
6 - 12	24.98	21.60	3.26	0.12	9.03	7.13	1.72	0.18
Cumulative total	50.48	43.10	6.46	0.92	35.52	29.63	4.91	0.98

Table 6. Concentrations of phorate residues in soil core samples collected on November 19, 1987, 57 days post application from a plot located in Del Norte County.

Depth (inches)	Phorate (ppm) expressed as total residue and phorate (P), sulfoxide (SO), and sulfone (SO2)							
	Core 1				Core 2			
	Total	P	SO	SO2	Total	P	SO	SO2
0 - 6	12.52	6.60	4.19	1.73	43.23	24.40	13.95	4.88
6 - 12	0.09	0.06	0.02	0.01	1.74	0.35	1.15	0.24
12 - 18	0.18	0.10	0.06	0.02	1.08	0.99	0.07	0.02
18 - 24	^a ND	ND	ND	ND	0.14	0.10	0.03	0.01
24 - 30	ND	ND	ND	ND	ND	ND	ND	ND
30 - 36	ND	ND	ND	ND	0.05	0.02	0.02	0.01
Cumulative total	12.79	6.76	4.27	1.76	46.24	25.86	15.22	5.16

a. None detected; minimum detectable level was 0.02 ppm for phorate, 0.009 ppm for phorate sulfoxide and 0.003 ppm for phorate sulfone.

Table 7. Concentrations of phorate residues in soil core samples collected on March 24, 1988, 182 days post application from a plot located in Del Norte County.

Depth (inches)	Phorate (ppm) expressed as total residue and phorate (P), sulfoxide (SO), and sulfone (SO2)							
	Core 1				Core 2			
	Total	P	SO	SO2	Total	P	SO	SO2
0 - 6	2.14	0.11	0.43	1.60	2.75	0.28	0.84	1.63
6 - 12	1.75	0.03	0.27	1.45	3.20	ND ^a	0.64	2.56
12 - 18	0.02	ND	ND	0.02	1.11	ND	0.24	0.87
18 - 24	ND	ND	ND	ND	0.21	ND	0.10	0.11
24 - 30	ND	ND	ND	ND	ND	ND	ND	ND
30 - 36	ND	ND	ND	ND	0.03	ND	0.01	0.02
36 - 42	ND	ND	ND	ND	ND	ND	ND	ND
42 - 45	ND	ND	ND	ND	0.04	ND	0.01	0.03
Cumulative total	3.91	0.14	0.70	3.07	7.34	0.28	1.84	5.22

a. None detected; minimum detectable level was 0.01 ppm for phorate, phorate sulfoxide and phorate sulfone.

Table 8. Concentrations of phorate residues in soil core samples collected on May 18, 1988, 237 days post application from a plot located in Del Norte County.

Depth (inches)	Phorate (ppm) expressed as total residue and phorate (P), sulfoxide (SO), and sulfone (SO ₂)							
	Core 1				Core 2			
	Total	P	SO	SO ₂	Total	P	SO	SO ₂
0 - 6	0.99	0.10	0.16	0.73	4.85	0.48	1.07	3.30
		a						
6 - 12	0.85	ND	0.07	0.78	2.58	ND	0.38	2.20
12 - 18	0.14	ND	ND	0.14	0.78	ND	0.17	0.61
18 - 24	0.26	ND	0.03	0.23	0.24	ND	0.10	0.14
	b							
24 - 30	--	--	--	--	ND	ND	ND	ND
30 - 36	--	--	--	--	ND	ND	ND	ND
36 - 42	--	--	--	--	ND	ND	ND	ND
Cumulative total	2.24	0.10	0.26	1.88	8.45	0.48	1.72	6.25

a. None detected; minimum detectable level was 0.01 ppm for phorate, phorate sulfoxide and phorate sulfone.

b. Not sampled.

Cumulative total concentrations of parent compound in replicate cores were reduced from an average value of 36.37 ppm at 1 day post to only 0.29 ppm at 237 days post application (Figure 7). Phorate sulfoxide concentrations increased from an average value of 5.69 ppm at 1 day post to 9.75 ppm at 57 days post application and declined to 0.99 ppm by the end of the study. Average concentrations of phorate sulfone increased from 0.95 ppm at 1 day post to 4.07 ppm at 237 days post application. Both compounds leached more deeply into the soil profile than the parent at 182 and 237 days post application (Tables 7, 8). In one of the replicate cores collected 182 days post application, phorate sulfone was found only 6 inches deeper than phorate while in the second core, both the sulfoxide and sulfone were found at 42-45 inches and the parent at only 12 inches deep. In the cores collected 237 days post application, both oxidation products were found 18 inches deeper than the parent, but occurred at a maximum depth of only 24 inches.

Rainfall patterns that occurred at the Del Norte plot were similar to those seen at the Humboldt County plot (Figure 4). Approximately 4.5 inches fell during the time between phorate application and the 57 day post application sampling. Then an additional 37 inches and 8 inches of rain fell prior to the soil sampling at 182 days and 237 days post application. Again, high rainfall probably was responsible for the leaching of phorate sulfoxide and sulfone into the soil.

Phorate has a water solubility of 500 ppm and a soil half-life of 52 days (1). It also has a relatively high affinity for adsorption to soil organic matter (Koc 3,200), a characteristic that reduces its potential to leach through soil (1, 2). However, phorate sulfoxide and phorate sulfone, which form rapidly

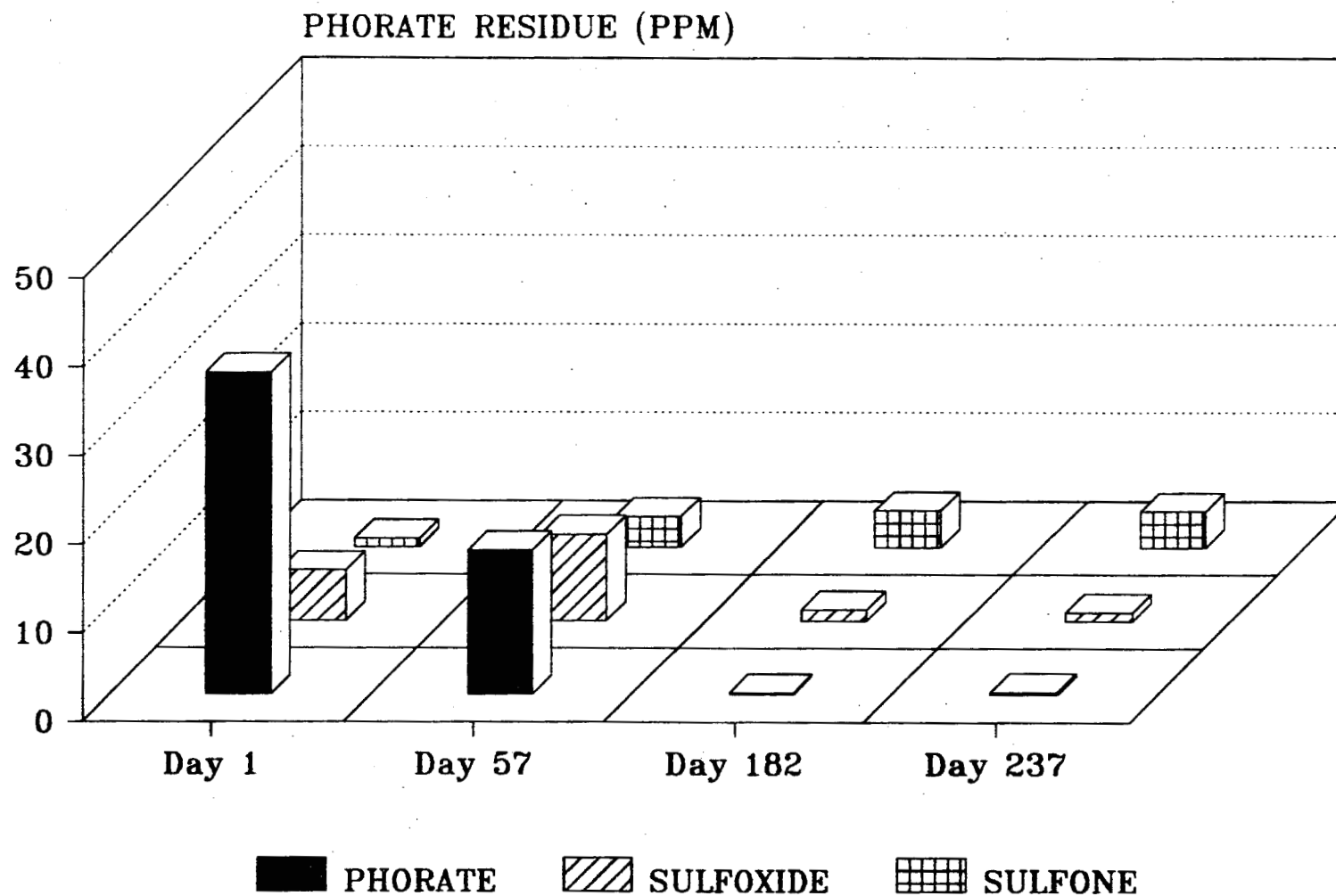


Figure 7. Average cumulative concentrations of phorate, phorate sulfoxide and phorate sulfone present in two soil cores collected on specified numbers of days post application from the test plot in Del Norte County.

after the parent is added to soil (2), are more soluble than the parent (3) and have considerably smaller Koc values (1). Therefore, they are considered to have a greater potential for leaching through soil. Laboratory and field studies have shown that some vertical movement of phorate compounds does occur in soil, particularly by the sulfoxide and sulfone components (3, 5).

In the present study, phorate was much less mobile than either the sulfoxide or sulfone in the two soils that were studied. This agrees with published information (3, 5) and was probably brought about by the lower water solubility of phorate and its greater affinity for adsorption to organic carbon in the soil. Both soils contained relatively high organic carbon contents. The sulfoxide and sulfone compounds leached more readily than the parent; low concentrations of both were found in some of the deepest samples collected. Further, phorate sulfoxide and sulfone leached more readily in the sandier soil present in the Humboldt County plot than in the more loamy soil in Del Norte County. The high amounts of rainfall that occurred in the two study areas were probably responsible for the degree of leaching that was observed even with the high organic carbon content in the soil. Although phorate is generally considered not to be a threat to groundwater, the sulfoxide and sulfone breakdown products that occur after application apparently do move downward through the soil under climatic conditions present in northwestern California.

Ethoprop

Ethoprop was applied to the plot in Humboldt County as a liquid formulation (Mocap 70 % L). Concentrations in the top 6 inches of soil averaged 8.3 ppm at 1 day post application, increased to 17 ppm by 57 days post, then decreased

to 2.2 and 2.9 ppm at 181 and 237 days post application, respectively (Table 9, Figure 8). Cumulative total concentrations in replicate cores averaged 9.22 ppm at 1 day post application and dropped to 4.53 ppm by the end of the study. In November, 57 days post application, by which time 3.5 inches of rain had fallen on the plot, ethoprop residues were detected at maximum depths of 12 and 18 inches. Later in March and May, 181 and 237 days post, additional leaching had occurred and residues were found at maximum sampling depths of 48 to 54 inches. These samplings followed periods in which 28 inches and 5.5 inches of additional rain fell on the plots. Concentrations of ethoprop found in soil below 18 inches were low and in the range of 0.01 to 0.07 ppm.

Soil coring performed in the Humboldt County plot in May was done without the use of a sleeve as was mentioned previously. A comparison of the results for March and May shows that although ethoprop was found at the same maximum soil depth in both months, there were more samples containing residues in May than in March. However, concentrations found below 2 feet deep were similar in both months.

In Del Norte County, ethoprop was applied to the plot as a granular material (Mocap 10 G). The average concentration in the top 6 inches of soil increased from 12.8 ppm at 1 day post to 33.2 ppm 57 days after application (Table 10, Figure 9). Concentrations decreased dramatically over the next several months and averaged 1.4 and 0.75 ppm at 182 and 237 days post application, respectively. Cumulative total concentrations in replicate cores averaged 19.76 ppm at 1 day post and dropped to 1.64 ppm by the end of the study.

Table 9. Concentrations of ethoprop residues in soil core samples collected at varying times post application from a plot in Humboldt County.

Depth (inches)	Ethoprop concentration (ppm), dry weight soil							
	1 Day Post (9/23/87)		57 Days Post (11/18/87)		181 Days Post (3/22/88)		237 Days Post (5/17/88)	
	Core 1	Core 2	Core 1	Core 2	Core 1	Core 2	Core 1	Core 2
0 - 6	6.88	9.78	15.90	18.10	2.13	2.32	2.42	3.36
6 - 12	0.63	1.15	0.21	0.15	1.64	2.28	0.75	1.95
12 - 18	-- ^b	--	0.03	ND ^c	0.88	0.27	0.10	0.21
18 - 24	--	--	ND	ND	0.07	0.04	0.01	0.03
24 - 30	--	--	ND	ND	ND ^d	ND	0.01	0.05
30 - 36	--	--	ND	ND	0.02	ND	0.03	0.01
36 - 42	--	--	--	--	ND	ND	0.02	0.04
42 - 48	--	--	--	--	0.02	ND	0.01	0.01
48 - 54	--	--	--	--	--	0.01	--	0.05
Cumulative total	7.51	10.93	16.14	18.25	4.76	4.92	3.35	5.71

a. Stainless steel sleeve was not used during collection of soil core.

b. Not sampled.

c. None detected; minimum detectable level was 0.02 ppm.

d. None detected; minimum detectable level was 0.005 ppm.

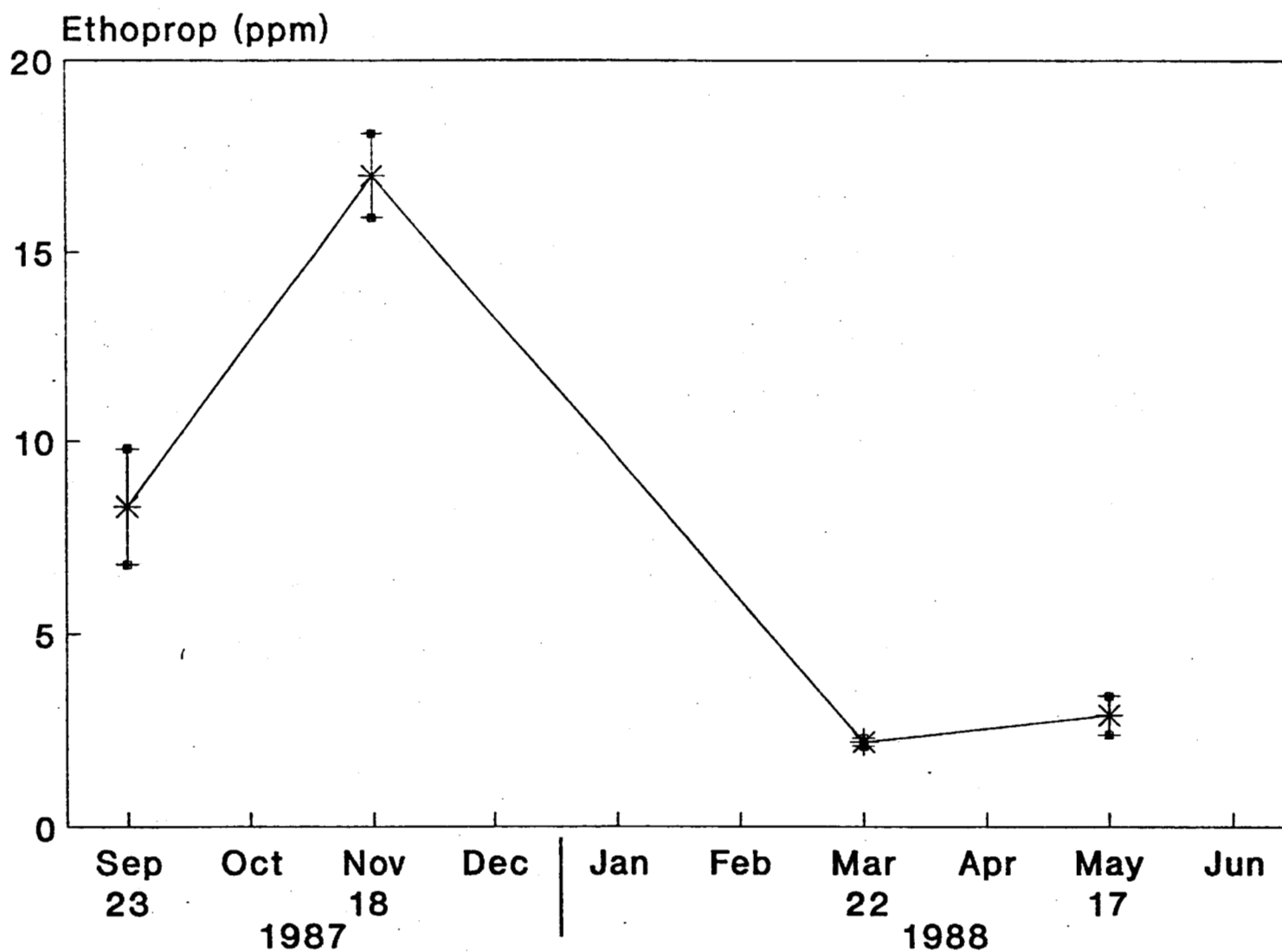


Figure 8. Mean and range of ethoprop residues present in the top 6 inches of soil in two cores collected on four sampling dates from the test plot in Humboldt County.

Table 10. Concentrations of ethoprop residues in soil core samples collected at varying times post application from a plot in Del Norte County.

Depth (inches)	Ethoprop concentration (ppm), dry weight soil							
	1 Day Post (9/24/87)		57 Days Post (11/19/87)		182 Days Post (3/24/88)		237 Days Post (5/18/88)	
	Core 1	Core 2	Core 1	Core 2	Core 1	Core 2	Core 1	Core 2
0 - 6	10.09	15.55	33.22	33.20	1.60	1.27	0.80	0.70
6 - 12	10.00	3.87	10.00	2.32	1.16	1.08	0.51	0.62
12 - 18	-- ^a	--	0.05	0.33	1.47	1.20	0.27	0.20
18 - 24	--	--	0.10 ^b	0.37	0.07 ^c	0.38	0.10	ND ^d
24 - 30	--	--	ND	0.16	ND	0.03	0.02	0.02
30 - 36	--	--	ND	0.07	ND	0.04	0.01	ND
36 - 42	--	--	--	--	0.02	0.04	0.01	ND
42 - 48	--	--	--	--	--	0.04	0.01	--
Cumulative total	20.09	19.42	43.37	36.45	4.32	4.08	1.73	1.54

a. Not sampled.

b. None detected; minimum detectable level was 0.02 ppm.

c. None detected; minimum detectable level was 0.01 ppm.

d. None detected; minimum detectable level was 0.005 ppm.

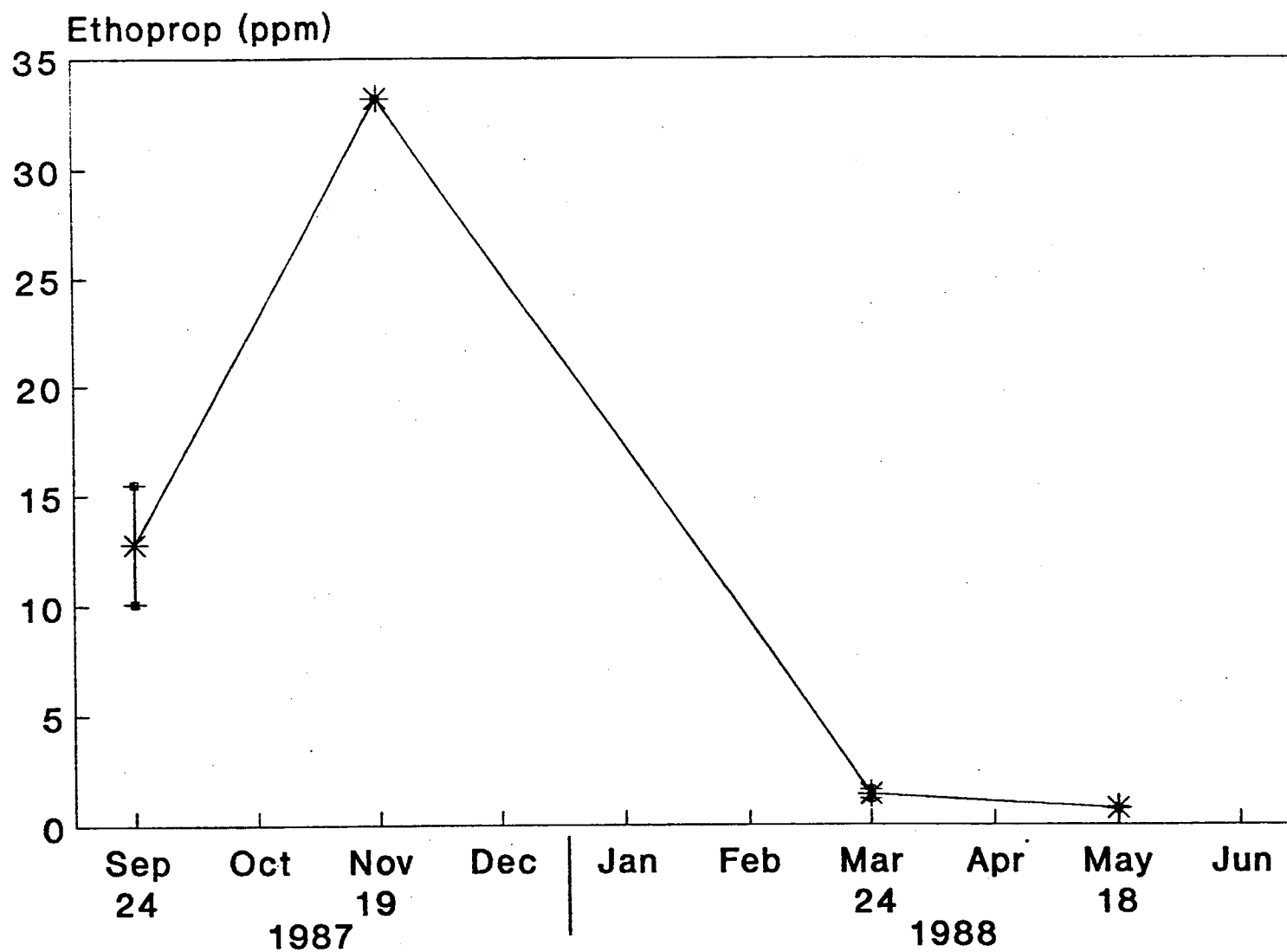


Figure 9. Mean and range of ethoprop residues present in the top 6 inches of soil in two cores collected on four sampling dates from the test plot in Del Norte County.

Leaching of ethoprop was evident after nearly 50 inches of rain fell during the 237 days subsequent to the application. Residues were found at maximum depths of 24 and 36 inches at 57 days post, 42 and 48 inches at 182 days post, and 30 and 34 inches at 237 days post application. Concentrations were low, ranging from 0.01 to 0.04 ppm in samples deeper than 30 inches collected in March or May.

Ethoprop is highly soluble in water (750 ppm), has a soil half-life of 40 days and a moderately low affinity for adsorption to organic carbon ($K_{oc} = 120$) in soil (1). These properties suggest that it should be mobile in soil.

However, studies on the leaching potential of ethoprop through soil columns under field conditions have shown that its downward movement is very limited (6), especially in soil with a high organic carbon content (7). Rainfall that occurred during the leaching study totalled approximately 14.5 inches, considerably less than the total in our test plot. In the same study, ethoprop persisted for a much longer period in an acid soil (pH 4.5 - 4.6) than in a neutral soil (pH 7.2 - 7.3).

Residues of ethoprop persisted in both test plots throughout the 237 day test period although levels were greatly decreased. Both the liquid formulation and the granular formulation yielded similar results. Leaching of ethoprop also occurred in both plots and similar low concentrations were found in the deeper soil profiles. The heavy rainfall that occurred during the test period was probably responsible for the observed leaching. These results indicate a greater potential for leaching for ethoprop than has been reported in the literature. A soil coring study of the movement of fenamiphos in lily bulb field soils in Del Norte County in 1985 yielded results much like those

obtained for ethoprop (8). The water solubility, Koc and soil half-life properties of fenamiphos are very similar to those of ethoprop (1). Under conditions of heavy rainfall present in Northwestern California, ethoprop may pose a threat to groundwater where shallow ground water conditions exist.

CONCLUSIONS

1. Phorate sulfoxide and phorate sulfone may pose a threat to shallow ground water due to leaching under conditions of high rainfall and porous soil. In Humboldt County, phorate was oxidized to phorate sulfoxide and sulfone after application to soil. Both oxidation products leached to depths of 48 to 54 inches (maximum sampling depth) into the sandy subsoil following rainfall that totalled 37 inches during the 8 month test period. Phorate parent compound leached much less readily and was confined to the top 12 to 24 inches of soil.

Leaching of phorate sulfoxide and sulfone was less severe in a loamy soil in Del Norte County even though nearly 50 inches of rain fell on the study plot. Phorate parent compound was mostly confined to the top 12 inches of soil there.

High amounts of rainfall leached the phorate oxidation products through shallow soil layers even though they contained relatively high (2.5-6.6 %) organic matter contents.

2. Ethoprop may pose a threat to shallow ground water due to leaching under conditions of high rainfall in Del Norte and Humboldt Counties. Ethoprop, applied as a liquid or a granular formulation, persisted for 8 months in soil in two test plots and leached to the maximum sampling depths (48 to 54 inches) following

rainfall totalling 37 and 50 inches. However, residues found deeper in the soil were at very low concentrations. Leaching occurred in spite of relatively high (2.5 to 6.6 %) organic matter contents in the top foot of soil.

RECOMMENDATIONS

1. Because of the high rainfall that occurs in bulb producing areas in Humboldt and Del Norte Counties, soil and well monitoring should be performed where either phorate or ethoprop are used extensively.
2. Studies to determine the leaching potential of phorate should include analysis of phorate sulfoxide and sulfone residues since they leach much more readily than the parent compound.
3. Studies should be conducted to find methods for reducing the potential for leaching of nematicides. Possible factors that could be altered are rates and timing of application, and use of split applications.

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APPENDIX A

CHEMICAL ANALYTICAL METHOD FOR THE ANALYSIS OF ETHOPROP, PHORATE, PHORATE SULFOXIDE, AND PHORATE SULFONE IN SOIL

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Original Date: 11/2/87
Supercedes: 2/22/88
Current Date: 7/22/88
Method #:

Ethoprop (Mocap), Phorate (Thimet), Phorate Sulfoxide,
and Phorate Sulfone in Soil

SCOPE:

This method is for the determination of residues of Ethoprop, Phorate, Phorate Sulfoxide and Phorate Sulfone in soil.

PRINCIPLE:

Soil samples are blended for uniformity and a representative sample (50 grams) is extracted twice with 100 ml of acetone. The extract is filtered and analyzed directly by gas chromatography with an NP detector.

REAGENTS AND EQUIPMENT:

1. Acetone- purity 99.9+%
2. Wide mouth amber pint jars.
3. Aluminum foil
4. Glass vials - seven milliliter volume with foil lined caps.
5. G10 Gyrotory^R Shaker or equivalent with bracket sizes to hold round amber pint jars.
6. Filter paper and glass filter funnels 90mm/100mm
7. Na₂SO₄ Anhydrous Granular Analytical Grade
8. Analytical standards of Ethoprop, Phorate, Phorate Sulfoxide, Phorate Sulfone.
 - a) Stock standards - 1mg/ml parent compounds; 100ug/ml-metabolites
 - b) Working standards - Dilute stock standards to several working standards to cover the linear ranges of the gas chromatograph and detector used (eg. 0.005ng to 5ng/ul).
9. Gas chromatograph equipped with NPD.
10. Column - Megabore- Carbowax 20M- 10 meters in length.
11. Top loading balance - 1000 gm or greater capacity.
12. Disposable aluminum dishes ~ 57mm Fisherbrand or equiv.
13. Analytical balance - four place capability.

ANALYSIS:

1. Weigh 50 grams + or - 0.1gm of the well mixed soil sample into a one pint amber glass jar on a top loading balance.
2. Add 100 ml acetone and close with screw cap lined with aluminum foil.
3. Place in bracket on the rotary table shaker and set speed to -200 RPM. Let mix 15 to 20 minutes.
4. Remove from shaker and let settle until liquid is mostly clear. Decant through filter paper and funnel containing ~1 inch Na_2SO_4 into any suitable container (fleaker, jar or flask) that will hold > 200 ml volume and allow adequate mixing.
5. Repeat steps 2 through 4 for a total of 2 extractions. Mix well.
6. A representative portion may be transferred to 7 ml screw cap vials for storage in freezer for later analysis. Direct sampling from container may be done if conditions permit immediate GC analysis.
7. Inject 2 ul portions of sample and standards into Megabore column coated with Carbowax 20M.
8. Measure and plot peak heights of standards at each attenuation used.
9. Determine % moisture in soil by weighing ~20gms into tared aluminum dish; drying in 105 C oven for > 12 hrs until constant weight; recording dry wt at room temp.
Use % dry wt to correct ppm found in "as received" soil to ppm dry soil.

EQUIPMENT CONDITIONS:

Gas Chromatograph - Perkin-Elmer Sigma 2

- | | | |
|------------------------|-------------------|-----------------|
| a) Column temperature: | Ethoprop | 95°C isothermal |
| | Phorate | 100°C " |
| | Phorate Sulfoxide | 150°C " |
| | Phorate Sulfone | 150°C " |
- b) Injector temperature: 240°C
c) Detector temperature: 300°C
d) H_2 -25 psi
e) Air -35 psi
f) He -7 psi
g) NP Bead mv adjusted to 50% chart response, atten. 8, A/Z off.

CALCULATIONS:

This GC had no integrator attachment, therefore off-scale peak responses had to be run at higher attenuations and appropriate standards run along side to allow graphs to be drawn and samples quantitated in nanograms. Direct proportional calculations of sample against stds were also done.

Peak heights of standards are linear at different levels.

Low level - 40 ppb - atten. 4
Medium level - 600 ppb - atten. 32
High level - 6000 ppb - atten. 256

200 ml solvent volume/50 gms soil sample - 0.5mg soil/2 ul injection.
Final volume for calculations same as original 200 ml; actual volume is less.

ppm = ng/mg soil = ng pest. found in 2ul injection (by comparison of peak heights to Std. curves) x 2

% Moisture = $100 \times \frac{(\text{wt of undried sample} + \text{dish}) - (\text{wt of dried sample} + \text{dish})}{(\text{wt of undried sample} + \text{dish}) - (\text{wt of dish})}$

100 - % Moisture = % dry wt soil

ppm (dry wt) = $\frac{\text{ppm (moist soil sample)} \times 100}{\% \text{ dry wt soil sample}}$

Samples are reported in ppm (dry wt soil) of Ethoprop, Phorate, Phorate Sulfoxide, & Phorate Sulphone.

DISCUSSION:

Important to keep injection volumes approximately the same. Standards should be made to allow this consistency.

Parent compounds of Mocap and Thimet may be run quite well on several different columns 3% OV-1, OV-17, 5% Phenyl Methyl, etc. However, it is critical to use Carbowax 20M or its equivalent, if any, to achieve the kind of separation of the Phorate metabolites witnessed under these conditions.

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METHOD 8140; ORGANOPHOSPHATE PESTICIDES in soil/sediment

1. EXTRACTION;

Label the cal id with the suffix '8140'.

Weigh 15 grams of sample into an 8-oz bottle with a teflon-lined cap.

Add 100 ml of 1:1 methylene chloride-acetone (v/v), and shake well to disperse.

Add 30 g of washed sodium sulfate, and shake to mix well.

Add the spiking solution if applicable. No surrogates are added.

Place the sonicator probe into the extract above the sediments, sonicate for 3 minutes at 50% power setting and pulse at 5.

Be sure the sonication mixes the soil/sediment with the solvent well during the three minutes. Do not allow the probe to touch the glassware; it could break and shatter the glass.

Decant the extract into a 250-ml erlenmeyer flask.

Sonicate the soil once more with 100 ml of methylene chloride-acetone and decant the extracts into the first erlenmeyer flask.

2. CONCENTRATION BY KUDERNA-DANISH METHOD for 8140;

Pour the extracts through filter paper in a filtering funnel into a K-D flask; a 10-ml concentrator tube attached to the 500-ml reservoir.

Allow the extract to drain. Rinse the sample flask with methylene chloride several times, and pour the rinsates through the filter paper each time into the KD flask.

Add several small teflon boiling chips and attach the 3-ball macro-Snyder column.

Prewet the column with methylene chloride, and concentrate the extract to ca 6 ml on the steam bath at ca 80-85 C.

Remove the KD flask from the bath and allow it to cool on the ring support for a minimum of 10 minutes.

CAREFULLY disassemble the concentrator tube and rinse the lower glass joint with small amount of methylene chloride.

Quantitatively transfer the extract to a 16-ml test tube and adjust the volume to 15 ml with methylene chloride; 15g/15ml.

Method 8140 continued-

3. ADJUSTMENTS of 8140;

Aliquot 2.0 ml of the water extract into an 8-ml test tube.

Reduce the extracts under nitrogen and exchange the solvent to isooctane several times.

Adjust the final volume to 2.0 ml; 2g/2ml.

Ready for GC-NP(TSD).

4. QUALITY ASSURANCE/CONTROL of 8140;

The method blank is mandatory and is performed for each set of matrix, and for every 20 samples.

The matrix spike and the matrix spike duplicate is optional and must be requested. They are performed for each matrix and for every 20 samples.

METHOD 8140; ORGANOPHOSPHATE PESTICIDES in soil

Spike the MS and MSD with 1.0 ml of 614/8140 spiking standard to the 15 g soil to yield:

	STANDARD CONCENTRATION	SPIKE LEVEL
phosdrin	10 ug/ml	330 ug/Kg (ppb)
thimet	10	330
diazinon	10	330
di-syston	10	330
dimethoate	10	330
fenthion	10	330
chlorpyrifos	10	330
methyl parathion	10	330
malathion	10	330
ethyl parathion	10	330
DEF	10	330
ethion	10	330
trithion	10	330
guthion	100	3,300

No surrogates are added; However, the P-surrogate does not interfere with the 614/8140 analysis.

DEG 6/1/88
8140

MOCAP (ETHOPROP) in soil/sediment

This method from the CDFA (rev. 11/2/87).

1. EXTRACTION;

Label the cal id with the suffix 'MOCAP'.

Weigh 50 grams of the well mixed soil into a cleaned 8-oz bottle.

Measure 100.0 ml of ethyl acetate, add to the soil, and close it with the teflon-lined screw cap.

Shake well to mix.

Add the spiking solution if applicable. No surrogates are added.

Place the extracts on the orbital shaker in horizontal position and shake for 1 hour at ca 250 rpm.

Remove from the shaker and allow it to settle.

Decant through Whatman 1 filter paper into a cleaned 8 oz jar. Do not rinse the filter paper.

Extract the soil once more with 100.0 ml of ethyl acetate on the orbital shaker for 30 minutes, and decant through the filter paper into the 8 oz jar. Again do not rinse the filter paper.

2. ADJUSTMENT;

No volume adjustments needed if the ethyl acetate was initially carefully measured.

Mix the solution well, and aliquot 16 mls into the 16-ml test tube: 50g/200ml. The excess may be discarded (check with the supervisor).

Ready for GC-NP(TSD). No screenings necessary.

4. QUALITY ASSURANCE/CONTROL of MOCAP;

The method blank is mandatory and is performed for each set of matrix, and for every 20 samples.

The matrix spike and the matrix spike duplicate is optional and must be requested. They are performed for each matrix and for every 20 samples.

MOCAP (ETHOPROP) in soil

Spike the MS and MSD with 0.8 ml of MOCAP spiking standard to the 50 g soil to yield:

mocap (ethoprop)	STD CONCN 500 ug/ml	SPIKE LEVEL 8,000 ug/Kg
------------------	------------------------	----------------------------

MOCAP (ETHOPROP) in soil/sediment continued-

No surrogates are added; However, the P-surrogate does not interfere with the 614/8140 analysis (MOCAP is an organo-phosphate pesticide).

Method modified 12/8/87: solvent changed from acetone to ethyl acetate.

DEG 12/8/87
DFA.MOCAP

APPENDIX B

RESULTS OF THE METHOD DEVELOPMENT AND QUALITY CONTROL ANALYSES FOR ETHOPROP, PHORATE, PHORATE SULFOXIDE, AND PHORATE SULFONE

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Table 1. Method Validation Data for the Ethoprop/Phorate Soil Study: Ethoprop.

Analyte: Ethoprop

Matrix: Soil

Detection Limit: 0.006 ppm (dry weight basis)

Lab: CDFA

Chemist: Mike Monier

Date: 12/4/87

Date Analyzed	CDFA Sample #	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	
10/21/87	E01	709	50	40	125	
10/21/87	E02	710	42	40	105	
10/21/87	E03	711	44	40	110	
10/21/87	E04	712	44	40	110	
10/21/87	E05	713	39	40	98	
10/21/87	E06	714	36	40	90	
10/21/87	E07	715	44	40	110	
10/21/87	E08	716	41	40	102	
10/21/87	E09	717	37	40	92	
10/21/87	E10	718	38	40	95	
10/30/87	101	778	510	600	85	
10/30/87	102	779	656	600	109	
10/30/87	103	780	644	600	107	
10/30/87	104	781	660	600	110	
10/30/87	105	782	690	600	115	
10/30/87	106	783	640	600	107	
10/30/87	107	784	640	600	107	
10/30/87	108	785	595	600	99	
10/30/87	109	786	640	600	107	
10/30/87	110	787	680	600	113	
10/30/87	111	788	5900	6000	98	
10/30/87	112	789	6400	6000	107	
10/30/87	113	790	5600	6000	93	
10/30/87	114	791	4100	6000	68	
10/30/87	115	792	6400	6000	107	
10/30/87	116	793	6240	6000	104	
10/30/87	117	794	6000	6000	100	
10/30/87	118	795	6600	6000	110	
10/30/87	119	796	6180	6000	103	
10/30/87	120	797	5900	6000	98	
	\bar{X}					
Matrix	Recovery	SD	LWL	UWL	LCL	UCL
Soil	103	10.5	82	124	72	135

UCL = Upper control limit, LCL = lower control limit

UWL = Upper warning limit, LWL = lower warning limit

UCL and LCL = mean \pm 3 SD, UWL and LWL = mean \pm 2 SD

Table 2. Method Validation Data for the Ethoprop/Phorate Soil Study: Phorate.

Analyte: Phorate

Matrix: Soil

Detection Limit: 0.012 ppm (dry weight basis)

Lab: CDFA

Chemist: Mike Monier

Date: 12/4/87

Date Analyzed	CDFA Sample #	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %
11/30/87	201	1019	42	40	105
11/30/87	202	1020	48	40	120
11/30/87	203	1021	42	40	105
11/30/87	204	1022	42	40	105
11/30/87	205	1023	42	40	105
11/30/87	206	1024	40	40	100
11/30/87	207	1025	42	40	105
11/30/87	208	1026	40	40	100
11/30/87	209	1027	40	40	100
11/30/87	210	1028	40	40	100
12/1/87	211	1029	660	600	110
12/1/87	212	1030	620	600	103
12/1/87	213	1031	612	600	102
12/1/87	214	1032	630	600	105
12/1/87	215	1033	612	600	102
12/1/87	216	1034	600	600	100
12/1/87	217	1035	650	600	108
12/1/87	218	1036	680	600	113
12/1/87	219	1037	620	600	103
12/1/87	220	1038	646	600	108
12/1/87	221	1039	5700	6000	95
12/1/87	222	1040	5850	6000	98
12/1/87	223	1041	5620	6000	94
12/1/87	224	1042	5720	6000	95
12/1/87	225	1043	5690	6000	95
12/1/87	226	1044	5650	6000	94
12/1/87	227	1045	5700	6000	95
12/1/87	228	1046	5780	6000	96
12/1/87	229	1047	5730	6000	95
12/1/87	230	1048	5680	6000	95

Matrix	\bar{X} Recovery	SD	LWL	UWL	LCL	UCL
Soil	102	6.2	90	114	83	121

UCL = Upper control limit, LCL = lower control limit

UWL = Upper warning limit, LWL = lower warning limit

UCL and LCL = mean \pm 3 SD, UWL and LWL = mean \pm 2 SD

Table 3. Method Validation Data for the Ethoprop/Phorate Soil Study: Phorate sulfone, Phorate sulfoxide.

Analyte: Phorate sulfone

Matrix: Soil

Detection Limit: 0.012 ppm (dry weight basis)

Lab: CDFA

Chemist: Mike Monier

Date: 12/18/87

Date Analyzed	CDFA Sample #	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	
12/8/87	1	1083	33	40	82	
12/8/87	2	1084	25	40	62	
12/8/87	3	1085	27	40	68	
12/8/87	4	1086	24	40	60	
12/8/87	5	1087	26	40	65	
12/8/87	6	1093	430	600	72	
12/8/87	7	1094	330	600	55	
12/8/87	8	1095	400	600	67	
12/8/87	9	1096	420	600	70	
12/8/87	10	1097	520	600	87	
\bar{X}						
Matrix	Recovery	SD	LWL	UWL	LCL	UCL
Soil	69	9.7	50	88	40	98

Analyte: Phorate sulfoxide

Matrix: Soil

Detection Limit: 0.012 ppm (dry weight basis)

Lab: CDFA

Chemist: Mike Monier

Date: 12/18/87

Date Analyzed	CDFA Sample #	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	
12/8/87	1	1078	35	40	88	
12/8/87	2	1079	35	40	88	
12/8/87	3	1080	29	40	73	
12/8/87	4	1081	39	40	98	
12/8/87	5	1082	39	40	98	
12/8/87	6	1088	460	600	77	
12/8/87	7	1089	400	600	67	
12/8/87	8	1090	450	600	75	
12/8/87	9	1091	430	600	72	
12/8/87	10	1092	490	600	82	
\bar{X}						
Matrix	Recovery	SD	LWL	UWL	LCL	UCL
Soil	82	11	60	104	49	115

UCL = Upper control limit, LCL = lower control limit

UWL = Upper warning limit, LWL = lower warning limit

UCL and LCL = mean +/- 3 SD, UWL and LWL = mean +/- 2 SD

Table 4. Ethoprop Quality Control Data, Winter 1987 through Spring 1988.

Analyte: Ethoprop

Matrix: Soil

Detection Limit: 0.006 ppm (dry weight basis)

Lab: CDFA

Chemist: Mike Monier

Date: 7/5/88

Date Analyzed	EHAP Sample #	Lab Sample #	Results (ppm)	Spike Level (ppm)	Recovery %	\bar{X} Recovery	SD	CV (%)
4/19/88	301-12	1703	0.898	1	89.8			
4/29/88	337-45, 347-8, 378, 381, 384	1704	0.803	1	80.3			
6/6/88	530-2, 534-40, 458, 461-66, 495-6, 500-4	2207	1.015	1	102			
6/13/88	474-6, 478, 529, 533, 481-92	2366	0.5946	0.6	99.1	92.8	9.82	10.6

Table 5. Phorate Quality Control Data, Winter 1987 through Spring 1988.

Analyte: Phorate

Lab: CDFA

Matrix: Soil

Chemist: Mike Monier

Detection Limit: 0.012 ppm (dry weight basis)

Date: 7/5/88

Date Analyzed	EHAP Sample #	Lab Sample #	Results (ppm)	Spike Level (ppm)	Recovery %	\bar{X} Recovery	SD	CV (%)
12/16/87	100-35	1060	1	1	100			
12/17/87	136-93	1064	0.95	1	95			
4/29/88	373-77, 379-83	1704	0.78	1	78*			
5/5/88	400-20	1705	1.012	1	101			
6/13/88	474-8, 529, 533	2366	0.6	0.6	100			
6/23/88	473, 494, 517-27	2410	0.472	0.4	118			
6/24/88	460, 463-8, 477, 493 497-8, 501-2, 528	2413	1.042	1	104	99.4	11.9	12.0
Analyte: Phorate sulfoxide			Detection Limit: 0.012 ppm (dry weight basis)					
12/16/87	100-35	1060	0.78	1	78			
12/17/87	136-93	1064	0.75	1	75			
4/29/88	373-77, 379-83	1704	0.796	1	79.6			
5/5/88	400-20	1705	0.979	1	97.9			
6/13/88	474-8, 529, 533	2366	0.6046	0.6	101			
6/23/88	473, 494, 517-27	2410	0.4	0.4	100			
6/24/88	460, 463-8, 477, 493 497-8, 501-2, 528	2413	1.15	1	115	92.4	15.0	16.2
Analyte: Phorate sulfone			Detection Limit: 0.012 ppm (dry weight basis)					
12/16/87	100-35	1060	0.67	1	67			
12/17/87	136-93	1064	0.65	1	65			
4/29/88	373-77, 379-83	1704	0.646	1	64.6			
5/5/88	400-20	1705	0.833	1	83.3			
6/13/88	474-8, 529, 533	2366	0.5948	0.6	99			
6/23/88	473, 494, 517-27	2410	0.42	0.4	105***			
6/24/88	460, 463-8, 477, 493 497-8, 501-2, 528	2413	0.929	1	93	82.4	17.1	20.7

* = Sample no. 1704 fell outside the lower control limit set for Phorate in soil at 83%.

*** = Sample no. 2410 fell outside the upper control limit set for Phorate sulfone in soil at 98%.

Table 6. Ethoprop/Phorate Soil Study Split/Confirmation Analyses, Winter 1987.

Analyte: Ethoprop

Matrix: Soil

Detection Limit (CDFA): 0.006 ppm

Detection Limit (Cal Labs): 0.04 ppm

Date collected: 11/18/87

Chemist (CDFA): Mike M.

Chemist (Cal Labs): Kirk P.

EHAP Sample #	Lab Sample #	CDFA * (ppm)	Cal Labs * (ppm)	\bar{X}	SD	CV (%)
152	1100	18.1				
167	32457-8		12.1	15.1	4.24	28.1
148	1098	0.152				
171	32457-12		0.14	0.15	0.01	5.8
157	1103	15.9				
162	32457-3		10.5	13.2	3.82	28.9
153	1101	0.205				
166	32457-7		0.14	0.17	0.05	29
149	1099	0.028				
170	32457-11		<0.04			
156	1102	<0.02				
163	32457-4		<0.04			

* All results reported on a dry weight basis.

Table 7. Ethoprop/Phorate Soil Study Split/Confirmation Analyses, Winter 1987.

Analyte: Phorate

Matrix: Soil

Detection Limit (CDFA): 0.012 ppm

Detection Limit (Cal Labs): 0.025 ppm

Date collected: 11/18/87

Chemist (CDFA): Mike M.

Chemist (Cal Labs): Kirk P.

EHAP Sample #	Lab Sample #	CDFA * (ppm)	Cal Labs * (ppm)	\bar{X}	SD	CV (%)
150 169	1114 3245-10	<0.02	<0.025			
151 168	1115 32457-9	29.1	28.8	29.0	0.212	0.733
154 165	1116 32457-6	2.06	0.988	1.52	0.758	49.7
155 164	1117 32457-5	0.36	0.395	0.38	0.02	5.3
158 161	1118 32457-2	0.19	0.132	0.16	0.04	25
159 160	1119 32457-1	20.2	23.2	21.7	2.12	9.78

*All results reported on a dry weight basis.

Table 8. Ethoprop/Phorate Soil Study Split/Confirmation Analyses, Winter 1987

Analyte: Phorate sulfoxide				Date collected: 11/18/87		
Matrix: Soil				Chemist (CDFA): Mike M.		
Detection Limit (CDFA): 0.012 ppm				Chemist (Cal Labs): Kirk P.		
Detection Limit (Cal Labs): 0.025 ppm						
EHAP Sample #	Lab Sample #	CDFA * (ppm)	Cal Labs * (ppm)	\bar{X}	SD	CV (%)
150	1114	<0.02				
169	3245-10		<0.025			
151	1115	4.14				
168	32457-9		8.25	6.20	2.91	46.9
154	1116	0.94				
165	32457-6		1.07	1.0	0.09	9.1
155	1117	0.147				
164	32457-5		0.53	0.34	0.27	80
158	1118	0.094				
161	32457-2		0.205	0.150	0.078	52.5
159	1119	3.2				
160	32457-1		10.6	6.9	5.2	75

Analyte: Phorate sulfone				Date collected: 11/18/87		
Matrix: Soil				Chemist (CDFA): Mike M.		
Detection Limit (CDFA): 0.012 ppm				Chemist (Cal Labs): Kirk P.		
Detection Limit (Cal Labs): 0.025 ppm						
EHAP Sample #	Lab Sample #	CDFA * (ppm)	Cal Labs * (ppm)	\bar{X}	SD	CV (%)
150	1114	<0.02				
169	3245-10		<0.025			
151	1115	2.16				
168	32457-9		4.13	3.15	1.39	44.3
154	1116	0.342				
165	32457-6		0.512	0.427	0.120	28.2
155	1117	0.083				
164	32457-5		0.222	0.153	0.098	64.5
158	1118	0.059				
161	32457-2		0.145	0.102	0.061	59.6
159	1119	2.02				
160	32457-1		7.07	4.55	3.57	78.5

* All results reported on a dry weight basis.

Table 9. Ethoprop/Phorate Soil Study Split/Confirmation Analyses, Spring 1988.

Analyte: Ethoprop

Matrix: Soil

Detection Limit (CDFA): 0.006 ppm

Detection Limit (Cal Labs): 0.04 ppm

Date collected: 3/22/88

Chemist (CDFA): Mike M.

Chemist (Cal Labs): Kirk P.

EHAP Sample #	Lab Sample #	CDFA* (ppm)	Cal Labs* (ppm)	\bar{X}	SD	CV (%)
318	1628	2.13				
315	40882-1		1.3	1.7	0.59	34
321	1631	1.64				
324	40882-6		1.8	1.7	0.11	6.6
313	1626	0.088				
317	40882-3		0.1	0.09	0.01	9.0
320	1630	2.32				
323	40882-5		2.9	2.6	0.41	16
314	1627	2.28				
316	40882-2		2.4	2.3	0.08	3.6
319	1629	0.272				
322	40882-4		0.39	0.33	0.08	24

*All results reported on a dry weight basis.

Table 10. Ethoprop/Phorate Soil Study Split Confirmation Analyses, Spring 1988.

Analyte: Phorate

Matrix: Soil

Detection Limit (CDFA): 0.012 ppm

Detection Limit (Cal Labs): 0.025 ppm

Date collected: 3/22/88

Chemist (CDFA): Mike M.

Chemist (Cal Labs): Kirk P.

EHAP Sample #	Lab Sample #	CDFA* (ppm)	Cal Labs* (ppm)	\bar{X}	SD	CV (%)
394	1636	3.81				
391	40882-10		2.3	3.1	1.1	35
388	1632	0.42				
385	40882-7		0.89	0.66	0.33	50
395	1637	0.135				
392	40882-11		<0.025			
389	1633	8.15				
386	40882-8		3.1	5.6	3.6	63
393	1635	0.241				
396	40882-12		0.1	0.17	0.10	59
390	1634	0.124				
387	40882-9		0.07	0.10	0.04	39

*All results reported on a dry weight basis.

Table 11. Ethoprop/Phorate Soil Study Split/Confirmation Analyses, Spring 1988.

Analyte: Phorate sulfoxide				Date collected: 3/22/88		
Matrix: Soil				Chemist (CDFA): Mike M.		
Detection Limit (CDFA): 0.012 ppm				Chemist (Cal Labs): Kirk P.		
Detection Limit (Cal Labs): 0.025 ppm						
EHAP Sample #	Lab Sample #	CDFA* (ppm)	Cal Labs* (ppm)	\bar{X}	SD	CV (%)
394	1636	5.17				
391	40882-10		4.4	4.8	0.54	11
388	1632	0.222				
385	40882-7		1.5	0.86	0.90	105
395	1637	0.964				
392	40882-11		0.92	0.94	0.03	3.3
389	1633	7.79				
386	40882-8		3.5	5.6	3.0	54
393	1635	3				
396	40882-12		2.2	2.6	0.57	22
390	1634	1.92				
387	40882-9		1.7	1.8	0.16	8.8
Analyte: Phorate sulfone				Date collected: 3/22/88		
Matrix: Soil				Chemist (CDFA): Mike M.		
Detection Limit (CDFA): 0.012 ppm				Chemist (Cal Labs): Kirk P.		
Detection Limit (Cal Labs): 0.025 ppm						
EHAP Sample #	Lab Sample #	CDFA* (ppm)	Cal Labs* (ppm)	\bar{X}	SD	CV (%)
394	1636	5.86				
391	40882-10		6.9	6.4	0.74	12
388	1632	0.716				
385	40882-7		1.6	1.2	0.63	54
395	1637	1.01				
392	40882-11		0.85	0.93	0.11	12
389	1633	6.43				
386	40882-8		3.6	5.0	2.0	40
393	1635	3.56				
396	40882-12		1.8	2.7	1.2	46
390	1634	2.21				
387	40882-9		1.3	1.8	0.64	37

*All results reported on a dry weight basis.

Table 12. Storage Dissipation Analyses for the Ethoprop/Phorate Soil Study: Ethoprop.

Analyte: Ethoprop

Matrix: Soil

Detection Limit: 0.006 ppm

Date of Report: 6/16/88

Chemist: (CDFA) Mike M.

Date samples prepared: 10/16/87

Lab Sample #	Day	Date Extracted	Date Analyzed	Amount Found (ppm)	Amount Added (ppm)	% Recovery	\bar{X}	SD	CV (%)
593	0	10/16/87	11/2/87	0.99	1	99			
594	0	10/16/87	11/2/87	0.83	1	83			
595	0	10/16/87	11/2/87	0.9	1	90	91	8.0	8.8
596	47	12/2/87	12/16/87	1	1	100			
597	47	12/2/87	12/16/87	0.98	1	98			
598	47	12/2/87	12/16/87	1.04	1	104	101	3.1	3.0
599	160	3/24/88	4/29/88	0.892	1	89			
600	160	3/24/88	4/29/88	0.914	1	91			
601	160	3/24/88	4/29/88	0.919	1	92	91	1.5	1.7
602	220	5/23/88	6/13/88	0.98	1	98			
603	220	5/23/88	6/13/88	0.839	1	84			
604	220	5/23/88	6/13/88	1.02	1	102	95	9.5	10

Table 13. Storage Dissipation Analyses for the Ethoprop/Phorate Soil Study: Phorate.

Analyte: Phorate

Matrix: Soil

Detection Limit: 0.012ppm

Date of Report: 6/16/88

Chemist: (CDFA) Mike M.

Date samples prepared: 10/16/87

Lab Sample #	Day	Date Extracted	Date Analyzed	Amount Found (ppm)	Amount Added (ppm)	% Recovery	\bar{X}	SD	CV (%)
593	0	10/16/87	11/2/87	0.99	1	99			
594	0	10/16/87	11/2/87	0.86	1	86			
595	0	10/16/87	11/2/87	0.96	1	96	94	6.8	7.3
596	47	12/2/87	12/16/87	0.783	1	78			
597	47	12/2/87	12/16/87	0.776	1	78			
598	47	12/2/87	12/16/87	0.846	1	85	80	4.0	5.0
599	160	3/24/88	4/29/88	0.45	1	45			
600	160	3/24/88	4/29/88	0.41	1	41			
601	160	3/24/88	4/29/88	0.48	1	48	45	3.5	7.8
602	220	5/23/88	6/13/88	0.34	1	34			
603	220	5/23/88	6/13/88	0.31	1	31			
604	220	5/23/88	6/13/88	0.26	1	26	30	4.0	13

Table 14. Storage Dissipation Analyses for the Ethoprop/Phorate Soil Study: Phorate sulfoxide, Phorate sulfone.

Analyte: Phorate sulfoxide
Matrix: Soil
Detection Limit: 0.012 ppm

Date of Report: 6/16/88
Chemist: (CDFA) Mike M.
Date samples prepared: 10/16/87

Lab Sample #	Day	Date Extracted	Date Analyzed	Amount Found (ppm)	Amount * Added (ppm)	% Recovery	\bar{X}	SD	CV (%)
593	0	10/16/87	11/2/87	<0.01					
594	0	10/16/87	11/2/87	<0.01					
595	0	10/16/87	11/2/87	<0.01					
596	47	12/2/87	12/16/87	0.08					
597	47	12/2/87	12/16/87	0.22					
598	47	12/2/87	12/16/87	0.11					
599	160	3/24/88	4/29/88	0.58					
600	160	3/24/88	4/29/88	0.44					
601	160	3/24/88	4/29/88	0.67					
602	220	5/23/88	6/13/88	0.656					
603	220	5/23/88	6/13/88	0.744					
604	220	5/23/88	6/13/88	0.794					

Analyte: Phorate sulfone
Matrix: Soil
Detection Limit: 0.012 ppm

Date of Report: 6/16/88
Chemist: (CDFA) Mike M.
Date samples prepared: 10/16/87

Lab Sample #	Day	Date Extracted	Date Analyzed	Amount Found (ppm)	Amount * Added (ppm)	% Recovery	\bar{X}	SD	CV (%)
593	0	10/16/87	11/2/87	<0.02					
594	0	10/16/87	11/2/87	<0.02					
595	0	10/16/87	11/2/87	<0.02					
596	47	12/2/87	12/16/87	<0.02					
597	47	12/2/87	12/16/87	<0.02					
598	47	12/2/87	12/16/87	<0.02					
599	160	3/24/88	4/29/88	<0.01					
600	160	3/24/88	4/29/88	<0.01					
601	160	3/24/88	4/29/88	<0.01					
602	220	5/23/88	6/13/88	<0.01					
603	220	5/23/88	6/13/88	<0.01					
604	220	5/23/88	6/13/88	<0.01					

*Samples were spiked with 1.0 ppm Phorate on 10/16/87.